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THESIS

1. Synthesis of NICKEL HALIDES in non-aqueous solvents.
2. Vapor pressure composition data.

Submitted by

Gary R. Argue

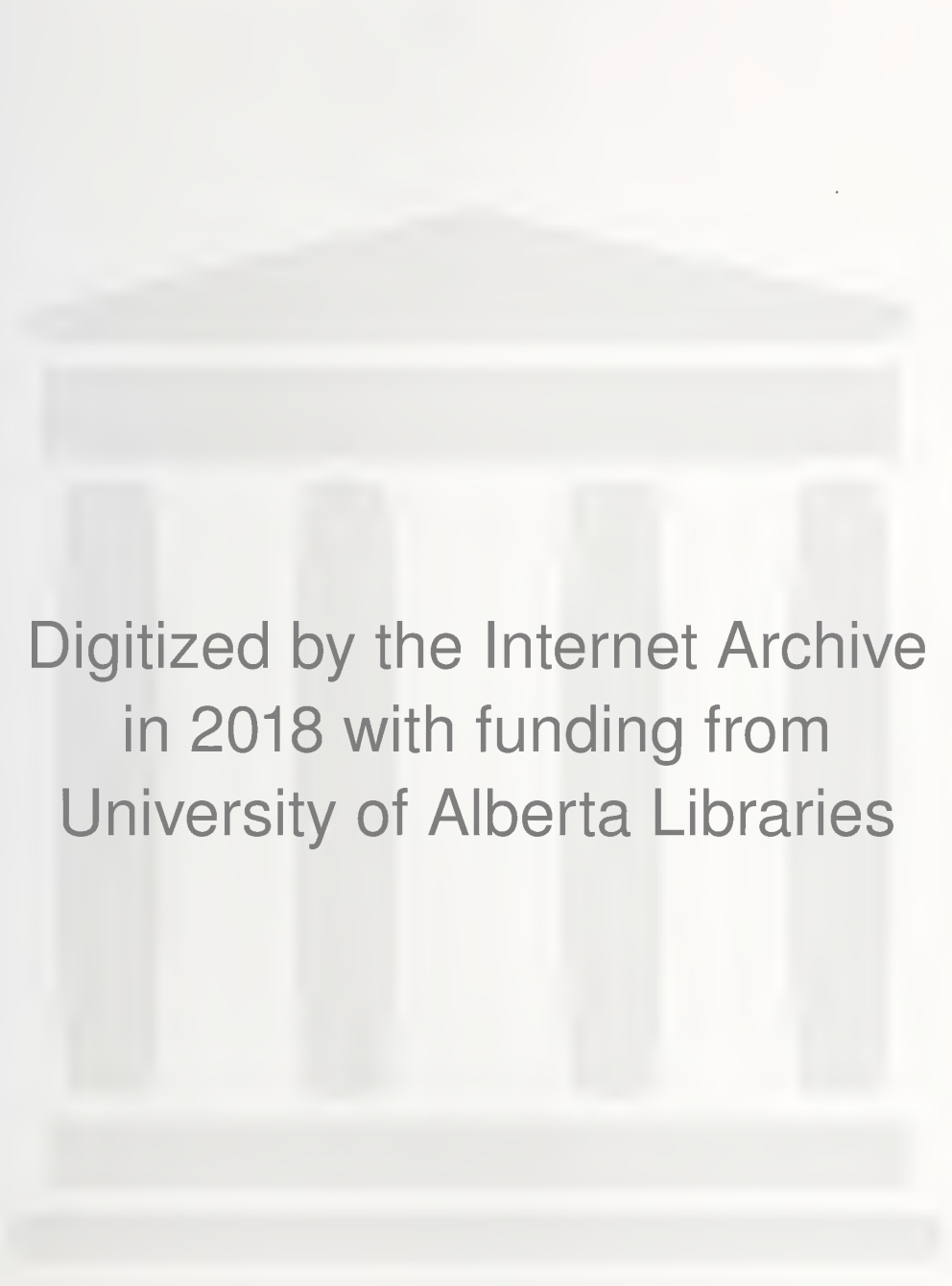
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THE UNIVERSITY OF ALBERTA

1. Synthesis of Nickel Halides in Non-aqueous Solvents
2. vapor Pressure Composition Data

A DISSERTATION

SUBMITTED TO THE SCHOOL OF GRADUATE STUDIES
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE
OF MASTER OF SCIENCE

FACULTY ARTS andSCIENCE
DEPARTMENT CHEMISTRY

BY

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EDMONTON, ALBERTA

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INTRODUCTIONS

SYNOPSIS

Production of anhydrous metal halides in general is a difficult and tedious undertaking. Most procedures require the use of high temperatures for both the actual reaction and the desolvation. It is the purpose of this work to follow up earlier attempts to produce metal halides in non-aqueous solvents and try to devise a general procedure.

Vapor pressure composition diagrams have been drawn in an effort to determine the metal halide-solvent complexes formed in each system. Vapor pressure measurements are made at different temperatures at the critical compositions. These are determined by the flat portions of the curves, which indicate stable complexes, and calculations are made to determine their heats of formation.

Molecular weight calculations are made to determine the species in solution. Some deviation from Raoult's law is noted in these calculations and some speculation is made as to the reason for them.

The work therefore, is divided into two main sections;

1. Synthesis.

2. Vapor pressure measurements and calculations on nickel iodide and bromide alcoholates.

PART 1 A

There are two general methods for preparing anhydrous transition metal halides. Both require the use of high temperatures at some stage.

(1) Place the finely ground metal in a tube and heat it to several hundred degrees and pass the halogen vapor over it. The reaction is incomplete and the salt has to be dissolved away from the elemental metal. Erdman (1) in 1839, prepared nickel iodide and Fischer (2) prepared nickel bromide similarly. Guichard (3) prepared these salts in vacuo. There are three main objections to this procedure;

- (a) the high temperature required for the reaction,
- (b) the high temperature required for the dehydration,
- (c) the yield is small since it is only a surface reaction,
- (d) the danger of hydrolysis during dehydration.

(2) React the corresponding metal oxide, carbonate or hydroxide with the corresponding halogen acid. In this case, heat is required for the dehydration of the hydrated salt.

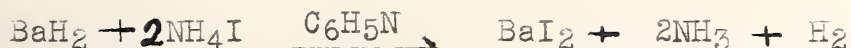
Because of these problems some attention has been given to the halide synthesis in organic solvents, but no general procedure has yet been reported.

The earliest work in this field was done by Ducelliez and Raynald (4) in 1914. They prepared bromides of cobalt, manganese, nickel and zinc by the attack of the halogen on the metal in anhydrous diethyl ether. The ether was allowed to evaporate and the salt crystallized out. Raynaud (5) proposed that the active brominating agent was hydrogen bromide produced by the reaction of bromine with ether.

Osthoff and West (6) in 1954, produced the chlorides of nickel, cobalt, manganese, chromium and zinc by the reaction of the metals with chlorine in anhydrous ethanol at reflux temperature. Part of the ethanol was removed by distillation and the precipitated salt filtered off, and washed with anhydrous diethyl ether. All manipulations were done under a blanket of dry nitrogen. The compounds so obtained were heated in vacuo for an hour to remove the excess ethanol.

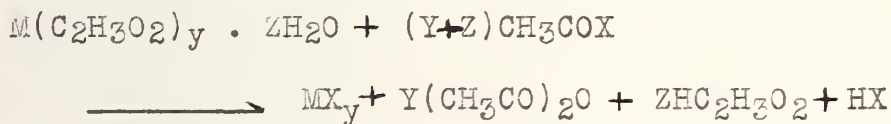
Recently, two other methods for the synthesis of metal halides have been reported.

(1) Taylor and Grant (7) prepared the iodides of metals of groups 1 and 2 by the reaction of the metal hydrides with iodine in anhydrous ether. An alternate method for barium iodide was presented as it was an exception in the ether procedure.



The excess barium hydride was filtered off and the pyridine removed in vacuo at 160° C.

(2) A procedure which deals with the metals of interest to this work was published in 1955 by Helvenston (8). He reacted the metal acetate hydrate with the acetyl halide in benzene.



This procedure is of general applicability but entails long reaction times, 12 hours in some cases, and required heating to 200°C. for 3 hours to remove the solvents.

Of these recent advances the procedure of Osthoff and West was thought to be the most workable and the easiest to adapt for the present purpose.

PART 2 A and B

INTRODUCTION AND THEORY

There has been much work done on the hydrates of the transition metal salts but little has been done on the alcoholates. Since this work deals with the nickel halides, references to previous work will be limited to them.

The hydrates of nickel bromide have been extensively studied by I. Bolschakaff (9) who found the 9, 6, and 3, hydrates and by Kusnetoff (10) who reported a dihydrate. A hexamine but no hydrates have been reported for nickel iodide. W. J. Jones(11) has done some work on the halides of cobalt, iron, and copper and nickel in methyl alcohol. He determined the solubility of cobalt chloride, cobalt bromide, and nickel bromide in methanol, and copper chloride in ethanol. He measured the dissociation pressures of the alcoholates formed and found that, of those examined, $\text{NiBr}_2 \cdot 6\text{CH}_3\text{OH}$ and $\text{CuCl}_2 \cdot 2\text{CH}_3\text{OH}$ both yielded the non-alcoholated salt upon further removal of alcohol. In addition, Jones found in contrast, that most of the salts of groups 1A and 2A exist in equilibrium as the non-alcoholated salts in their respective saturated solution.

The method employed by Jones for his study of the

alcoholates was to pass dry air through the system and measure the amount of alcohol taken up by the air. The vapor pressure of the system could then be calculated from the equation

$$\frac{P}{P'} = \frac{v}{V+v}$$

where P is the dissociation pressure of the alcoholate in mm. of mercury, v and V are the respective volumes of alcohol vapor and dry air in the mixture.

No reference was found to work on alcoholates by the method used here. No reference was found regarding molecular weight calculations on these compounds in alcohol solutions. Molecular weight calculations of aluminum halides in aromatic solvents were done by Brown and Wallace (12) who found that these systems behaved ideally. There was no mention of behaviour in donor solvents.

In the last few years, especially 1955, there has been considerable interest in the association and ionization of electrolytes in non-aqueous solvents. In aqueous media ionization usually implies dissociation and dissociation implies ionization. In non-aqueous media this is not necessarily the case. Species which are completely ionized in water are necessarily completely ionized in non-aqueous solvents but in the latter case, separation into independently

mobile ions (dissociation) is not necessarily complete. There may be, instead, an equilibrium between ionized molecules (ion pairs) and separated ions.

This dissociation equilibrium is dependent on many factors. Kraus (13) has given an extensive discussion of these factors. He has shown, by work with some alkyl ammonium salts in various solvents that Bjerrum's (14) postulate that the internuclear distance in ion pairs is constant, is not completely true. Instead he found that the parameter which Bjerrum associated with internuclear distance varied with the dielectric constant of the solvent, the temperature of the system, and the concentration of the salt. A plot of $\log K$ (dissociation constant) vs $\log D$ (dielectric constant) showed a point above which K increased asymptotically. Then, for all values greater than the critical D value, the ions of appropriate parameters are completely associated. He stated that, "for every typical salt in any solvent of dielectric constant such association occurs in less concentrated solution. there is a concentration C_m at which the degree of association is a maximum."

The size of the anions has a marked effect on K and it is shown by table 1.

Variation of K with anion size

TABLE 1

Salt	$K \times 10^4$	$A \times 10^8$	solvent	D
Bu ₄ NCl	22.8	3.07	acetone	20.5
Bu ₄ NBr	32.9	3.55	"	"
Bu ₄ NI	64.8	4.77	"	"

THEORETICAL PART

PART 2 B

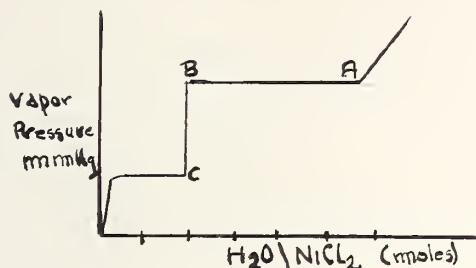
THE PHASE RULE

Gibbs has stated that for a system of C components and P phases, $F = C + P - 2$ where F equals the number of degrees of freedom for the system. It can be shown, by means of this rule that a two component, one phase system has three degrees of freedom; i.e. requires three variables for a complete description of the system. Thus a three dimensional diagram would be required for a complete graphical representation of the system. For many purposes a two dimensional diagram is more convenient to use. Such a diagram may be obtained by holding one of the variables fixed and studying the system as a function of the other two. In this work then, the isothermal variation of pressure with composition will be studied. A series of isotherms will be run at critical concentrations, and the variation of pressure with temperature data used for the calculation of the heat effects in the system.

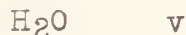
The application of the phase rule to the interaction of a metal salt with a solvent is well illustrated by the data of Eprham for the nickel chloride-water system shown diagrammatically in figure 1.

Vapor pressure composition diagram for the $\text{NiCl}_2\text{-H}_2\text{O}$ system.

FIGURE 1



There are three phases in equilibrium-

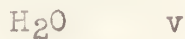


$$F = C + P + 2$$

$$F = 2 + 2 - 3$$

$$F = 1$$

Then, from A-B the composition is allowed to vary while the pressure remains constant. At B, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ is all converted to $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$ and the pressure drops to C. At C there are two phases in equilibrium



$$F = C + P + 2$$

$$F = 2 + 2 - 2 = 2$$

Thus from B - C there are two degrees of freedom. The pressure varies and the temperature can vary while the composition remains constant. At this point the

vapor pressure of any one solvate cannot be explicitly specified. The cycle repeats itself until the number of phases is reduced to one, namely NiCl_2 .

Therefore it can be seen that the stepwise variation of vapor pressure with composition affords a sign of solvate formation, and through the systematic measurement of the vapor pressure one can detect and ascertain the properties of these solvates.

VAN'T HOFF ISOCHORE

The Van't Hoff isochore can be expressed

$$\frac{d \ln K}{dt} = \frac{\Delta H_v}{RT^2} \quad \Delta H \text{ per mole}$$

For the reaction



the equilibrium constant is just the pressure of the alcohol over the solid. Substituting $K_p = P$

$$\frac{d \ln P}{dt} = \frac{\Delta H_v}{RT^2}$$

By measurements of the dissociation pressure of the solvate at a series of temperatures the heats of formation of the solvate can be determined. Then by integrating the Van't Hoff isochore with respect to temperature, gives

$$\ln P = - \frac{H_V}{R} \left[\frac{1}{T} \right] + C$$

$$\log P = - \frac{H_V}{2.3R} \left[\frac{1}{T} \right] + C$$

A plot of $\log P$ vs $\frac{1}{T}$ should give a straight line graph with slope $-\frac{H_V}{2.3R}$ and an intercept equal to C , where H_V is the heat of vaporization of the solvent from the solid.

W. J. Jones found that this equation was applicable to alcoholates over a moderate temperature range. Confining the measurements to a moderate temperature range is necessary because H_V is assumed to be constant, and over a large temperature range it is not. The value obtained from these calculations is the heat of vaporization of the alcohol from the halide. These values, when combined with the heats of vaporization of the pure solvent give the heat of dissociation of the solid complex into the solid salt and liquid alcohol.

CALCULATION OF MOLECULAR WEIGHTS

Assuming that the salts behave ideally, the molecular weights in solution can be calculated from Raoult's law.

$$P = P^0 N_1$$

P = vapor pressure of solution

P^0 = vapor pressure of pure solvent

$$\Delta P = P^0 - P$$

$$\Delta P = P^0 - P = P^0 - P^0 N_1$$

N_1 = mole fraction of solvent

$$\Delta P = P^0 (1 - N_1)$$

N_2 = mole fraction of solute

$$\Delta P = P^0 N_2$$

M_1 = molecular weight of solvent

M_2 = molecular weight of solute

$$\begin{aligned} N_2 &= \frac{\frac{W_2}{M_2}}{\frac{W_2}{M_2} + \frac{W_1}{M_1}} \\ &= \frac{W_2/M_2}{n + W_2/M_2} \end{aligned}$$

$$\text{Then } M_2 = \frac{1}{n} \left[\frac{WP}{\Delta P} - W \right]$$

These calculations are valid if the solute behaves ideally and there is no dissociation. Dissociation gives values of M_2 which vary. If dissociation is complete, each ion acts like an individual molecule. As the concentration of the solution is increased and the dissociation constant is diminished, the recombined ions effectively vary the calculated molecular weights until association is complete.

Solvent which is associated with the salt is essentially removed from the solution, and before calculations can be made, a correction has to be made. This is done simply by subtracting the moles associated from the moles in solution.

PART 1 B

EXPERIMENTAL PART

1. Synthesis of anhydrous metal halides

A Nickel Bromide

Twenty three grams of bromine were added, dropwise, to 5 gm. of nickel (Sheritt Gordon 98.6% Ni powder) in 100 ml. of refluxing anhydrous diethyl ether(34.5°C). The reaction did not go to completion even when 30 gm. of excess bromine were added. The mixture was allowed to mix over night but the reaction was still incomplete. The precipitated NiBr_2 (yellow brown) was filtered, washed with anhydrous diethyl ether and dried on the pump. There was some unreacted Ni in the precipitate.

It was then decided to try the reaction in anhydrous ethanol since in this solvent, the solubility of the metal chloride was great enough, that the reaction of the metal with chlorine was complete within one hour. Thirty grams of bromine were added, dropwise, to a magnetically stirred mixture of 8 gm. of Ni in 100 ml. of refluxing anhydrous ethanol(B.P.+78.3°C R.I.-1.3622). The reaction went smoothly and after 1 hour there was no sign of unreacted Ni in the flask. The mixture was dark emerald green and there was no precipitate present. The solution was then reduced to half volume by distillation and the resulting orange

precipitate was washed with anhydrous diethyl ether and dried on the pump. The product was very heterogeneous and there was some sign of decomposition.

The distillate was very lachrymatory and it gave a positive Benedict test for aldehyde. The presence of acetaldehyde was assumed. An ester-like odor was noticed in the higher boiling fraction but no chemical test was made to determine the presence of an ester.

This method of isolation was then discarded as unsatisfactory and two different methods were attempted.

(1) After the ethanol solution was concentrated to the point of precipitation, 100 ml. of anhydrous diethyl ether were added. A yellow brown precipitate was obtained which increased in quantity upon standing. The precipitate was collected by filtration, washed with ether and dried on the pump. It analysed 98% NiBr_2 .

(2) After the ethanol solution was concentrated to the point of precipitation by distillation, 100 ml. of anhydrous toluene were added and the distillation continued. The azeotrope distilled at 76.1°C . A yellow precipitate was obtained. The analysis showed 98% NiBr_2 .

At this point it was decided to modify the ether procedure to see if the ethanol side reactions' products could be eliminated. After the reaction in ether was finished (see above), the salt was filtered, washed with ether and dissolved in 100 ml. of ethanol. This solution was filtered to remove the excess Ni powder, and the filtrate was treated with 100 ml. of toluene and distilled. The precipitate obtained as in procedure 2, was filtered, washed with ether and dried on the pump. It analysed 97% NiBr_2 .

B Nickel Iodide

The synthesis of NiI_2 was attempted by the procedures described above. The reaction of nickel with iodine was found to be incomplete when diethyl ether was used as the solvent and the product was contaminated with unreacted metallic nickel.

The reaction was found to go to completion in anhydrous ethanol but some decomposition was found during the reduction of volume of the solution to induce crystallization. However, ethanol did appear to be the most advantageous reaction medium.

Thirty-four grams of iodine dissolved in anhydrous ethanol were added to 8 gm. of Ni in 100 ml. of refluxing ethanol. The reaction was slower than with bromine, but proceeded to completion in about 2 hours. The green ethanolic solution was reduced to half volume by distillation, and then 100 ml. of anhydrous toluene were added. The azeotrope distilled off as before and black NiI_2 precipitated out. The solid was filtered, washed with ether and dried on the pump. The compound analysed 98.4% NiI_2 .

The preparation of the bromides of Cu, Fe, Mn and Zn, and the iodides of Cu and Fe was attempted by R. Richardson using the ethanol-toluene procedure. Only CuBr_2 and CuI were obtained. CuBr_2 analysed 99% but no analysis was made of the iodide. Iron yielded tarry substances in both cases. This probably indicates the formation of some complex, possibly of the MX_2HX -toluene type. This possibility is to be investigated at a later date. The Mn and Zn bromides were not obtained pure by R. Richardson (16) but it is thought that they may yield to future work.

PART 2 C

APPARATUS

The vacuum apparatus used for this work was of quite elementary design. It was essentially a sample equilibrium section with a manometer attached, and a condensation tube section with a McLeod gauge. The pressure of residual gas in the system could be reduced below 10^{-5} mm. of Hg by a mercury diffusion pump. The system is shown diagrammatically in figure 2.

It was found that the operations in the vacuum system were more efficiently conducted when agitation was provided. In the original apparatus, a stirring mechanism was devised, which was elementary in design, and efficient. The stirring mechanism consisted of a small bar of metal enclosed in glass, with a long glass rod attached to it. The stirring action was obtained by lifting and dropping this stirrer by opening and closing the circuit of a solenoid, which was placed around the bar magnet on the upper end of the stirrer. Stirring efficiency was increased by flattening the lower end of the glass rod.

The solenoid circuit is shown in figure 3. The circuit breaker was a fifty-five cent Christmas tree light flasher. This made and broke the current through a variac-solenoid circuit about 3 times every 10 seconds.

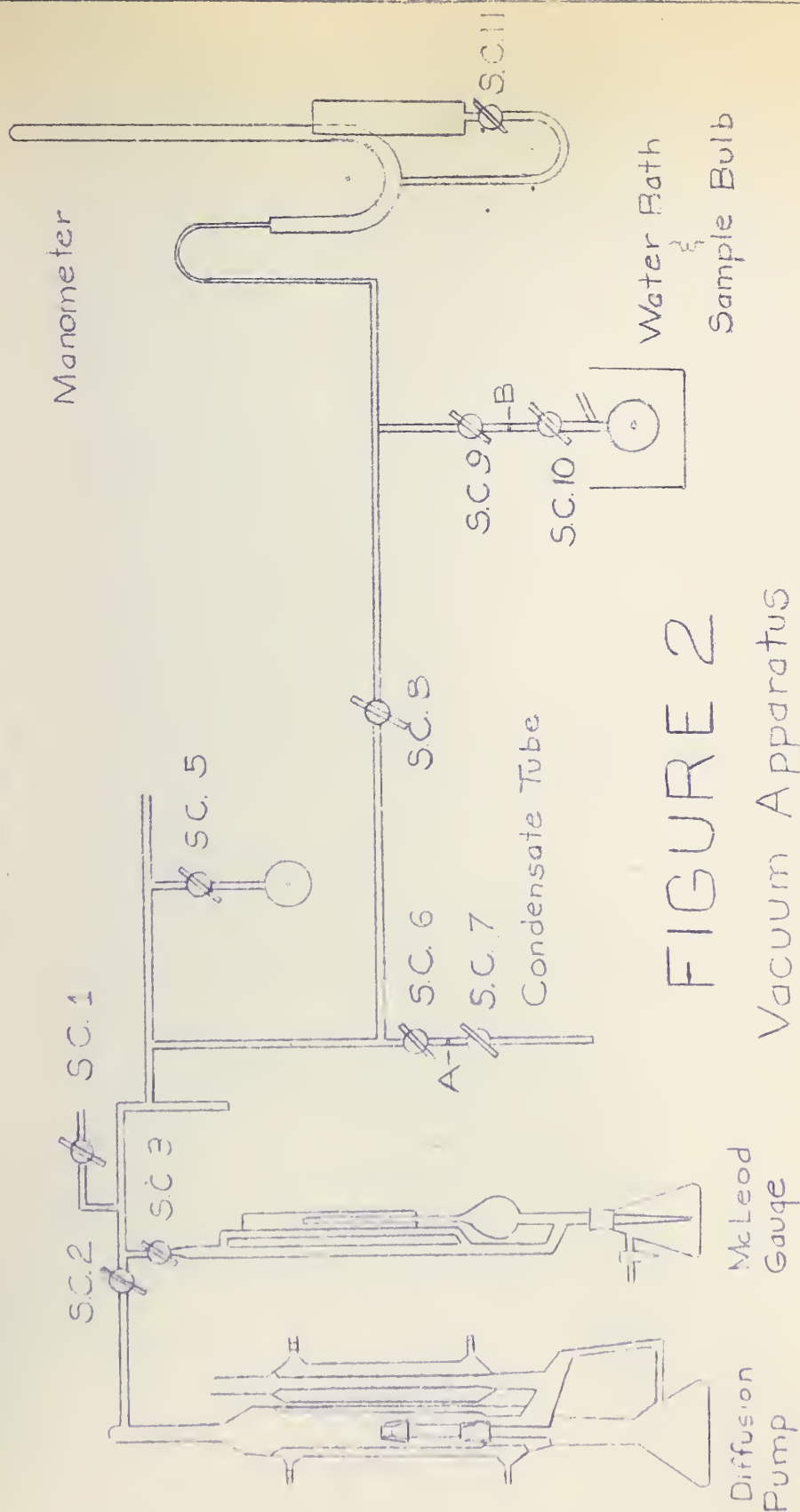


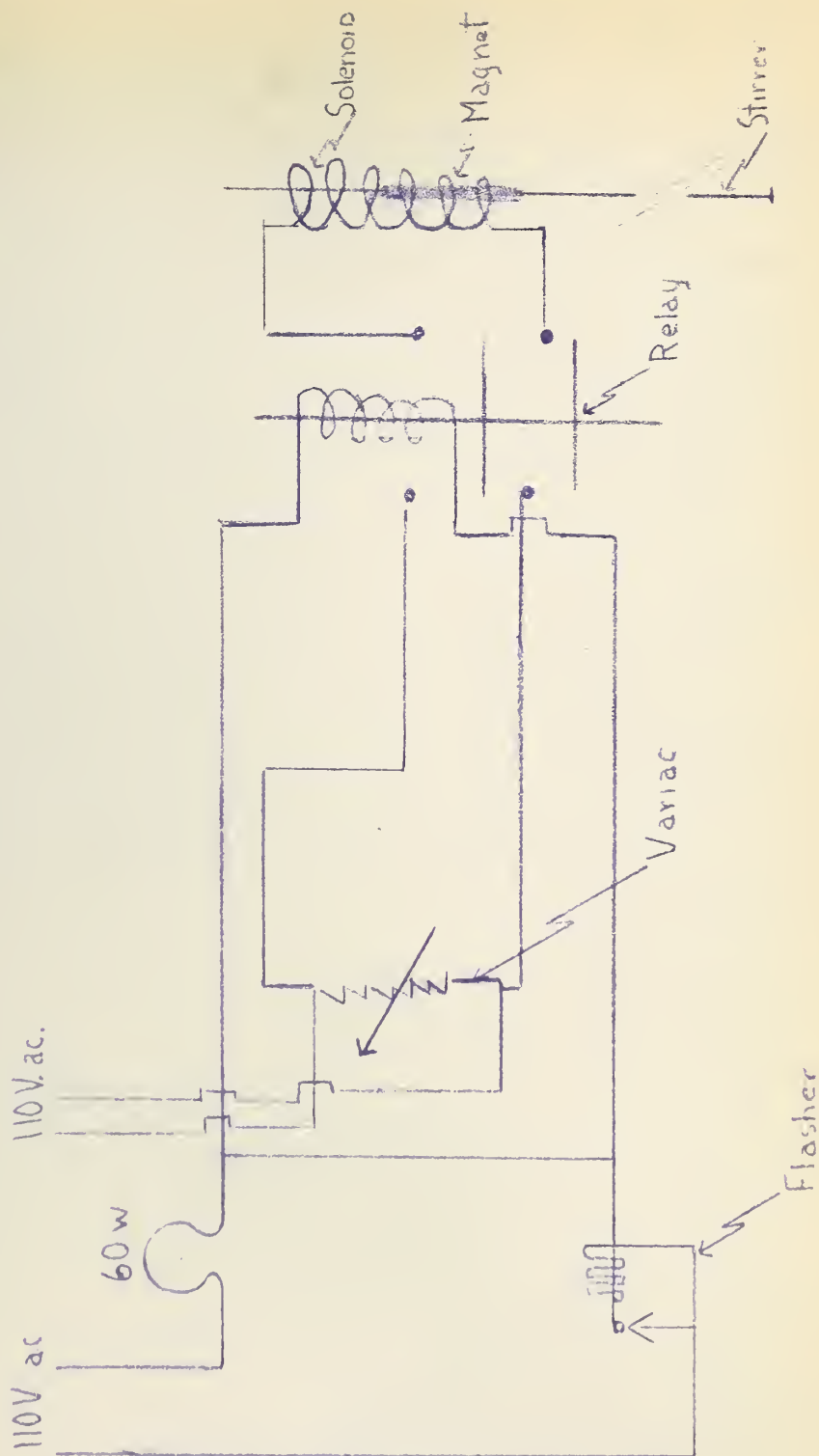
FIGURE 2

Vacuum Apparatus

for work on the systems:



Figure 3
Magnetic Stirrer Circuit Diagram



The solenoid was made of 1200 turns of #30 enamelled copper wire on a $1\frac{3}{4} \times \frac{3}{4}$ " spindle.

Some difficulty was encountered with material balances so a different type of sample tube was designed. This new sample tube made it impossible to use the stirrer described above because of the introduction of a stop cock. Instead, the solution was stirred magnetically by means of a magnet made from a small nail sealed in glass. The constant temperature bath, which was mounted on a car screw jack, was lowered and a magnetic stirrer placed under the bulb stirred the solution. This method of agitation was very satisfactory.

The bath was thermally controlled by a Fischer Unitized bath electronic control unit to $\pm 1^{\circ}\text{C}$.

PART C

PROCEDURES

(1) In the original procedure, a weighed sample of solid was placed in the bulb, a weighed amount of alcohol added to it and time was allowed for dissolution and equilibration. The vapor pressure of the system as indicated on the mercury manometer was then read with a cathetometer until two successive readings, spaced 10 minutes apart, gave identical values. Stop-cock #2 was closed, S.C.#8, #6 and #7 were opened and some of the alcohol was allowed to distill into the condensate tube which was cooled with a Dry Ice-acetone bath. S.C. #8 was closed and the completeness of transfer was checked by measuring the pressure in the system with the McLeod gauge. S.C. #6 and #7 were then closed and S.C. #2 was reopened. The condensate tube was removed and weighed. It was replaced at A and the alcohol removed by the pump. The tube was reweighed and the difference was the weight of alcohol. Thus the composition of the system could be determined at any time from the original amount of solute used and the total amount removed. In this way vapor pressure composition diagrams could be constructed for the system. It was found that along with the first three samples considerable noncondensable gas was removed. This no

doubt, accounted for the poor material balances obtained, since noncondensable gases make quantitative transfer extremely slow. The noncondensable gas was probably air dissolved in the solvent. It was then deemed necessary to resort to a different attack.

(2) The solid sample was introduced via the side arm on the above mentioned sample tube. The arm was then sealed, the tube evacuated and weighed. The alcohol was introduced by filling the upper part of the tube and opening S.C. #10, thus allowing the alcohol to be sucked in. Successive amounts of alcohol were removed until no trace of noncondensable gases were found. The amount of alcohol left at this point, determined by the difference in weight of the sample and bulb and the weight of the bulb, sample and alcohol, was the starting concentration for a run. The concentration for each run is expressed in moles of alcohol per mole of the salt.

The sample tube was then replaced on the line, a liquid air bath placed around it, S.C. #9 and S.C. #10 opened, and the system evacuated. The mercury level in the manometer was raised and S.C. #8 closed. The cold bath was then removed, and the 25° temperature bath raised around the sample and time was allowed

to equilibrate. As long as no solid was present, two identical readings five minutes apart were sufficient to indicate equilibrium. As solid appeared, equilibrium was attained more slowly and identical readings at 20 minute intervals were required. After equilibrium was reached, S.C. #8 was opened and a portion of the alcohol distilled off. S.C. #9 and #10 were then closed, and the sample tube removed from the line. After the silicone grease was removed by wiping the ground joint with CCl_4 , the tube was dried and weighed. The difference between this and the weight of the tube and sample only, was the weight of alcohol remaining. The tube was then replaced on the system and S.C. #9 was opened. When, according to the McLeod gauge, the pressure in the system had been reduced to 10^{-6} mm. Hg, S.C. #8 was closed and S.C. #10 opened, and the system again allowed to come to equilibrium. This procedure was repeated until the vapor pressure was reduced below the measurable range.

This method was further modified, when it was found that the results were still inconsistent. In the final procedure, 1mmole of elemental nickel and 1.2 mmole iodine were placed in the sample tube with the magnetic stirrer, the tube was sealed and evacuated, and anhydrous ethanol added to the sample as described above. The ethanol was purified first with sodium, then boiling the

azeotrope of benzene and water off, and finally distilling the ethanol from sodium and diethyl phthalate just before use. This method eliminated the contact with air which had seemed to contaminate the previous samples so badly. The reaction went to completion. The excess halide and ethanol were removed and the sample desolvated to a constant weight. This indicated that the sample was anhydrous. Material balances here were good. Anhydrous ethanol was again added and the sample dissolved as previously described.

MEASUREMENT OF VAPOR PRESSURES AT DIFFERENT TEMPERATURES

At the point in question the vapor was condensed with liquid air. The bath of the appropriate temperature below room temperature then replaced the liquid air bath, and two hours allowed for the system to reach equilibrium. The temperature of the baths was measured by a thermometer which was calibrated at 0°C . with ice and at 31.4°C . (15)

The temperatures above room temperature were obtained by use of the water bath, which was controlled by the Fischer bath control unit. It was found that a smooth curve could be obtained with increasing temperature but with decreasing temperature the agreement was not satisfactory. Identical results could be

obtained only if some ethanol was allowed to distill from the system at the lowest temperature, and the equilibrium pressures again measured at increasing temperatures.

CONDUCTIVITY MEASUREMENTS

A conductivity bridge (Industrial Instruments Inc. Model RC) was used for these measurements. The cell constant was determined by measurements on a standard solution of 0.1 M KCl.

PART 2 D

Measurements and Calculations of the System Ethanol-Nickel Bromide

The alcohol purified as previously described was checked for purity on the Abbe Ziess refractometer. The distillate was removed and condensed as described in procedure one. It was also checked and no appreciable deviation was noted.

TABLE 2

Refractive indices of ethanol

	observed	literature
Sample ethanol	1.3622	1.3618 I.C.T.
Distillate ethanol	1.3620	

The nickel iodide was analysed after the runs in ethanol and diethyl ether were completed. Particles of glass wool from the plug in the upper portion of the sample tube contaminated the solid. The values given are mmoles found.

TABLE 3

Sample No.	Iodine Mmole	Method of Analysis	Nickel Mmole	Method of Analysis	Mole Ratio
1	0.890	Volhard	0.381	KCN AgNO ₃	NiI ₂ 2.020
2	0.931	Volhard	0.928	KCN AgNO ₃	NiI ₂ 2.002

Runs #1 and #2

There were some inconsistencies in the data obtained in these early runs. These are shown in tables 4 and 5 and in figure 4.

From the graphical representation of these results in figure 4, a divergence of the data is noted at the point where solid appears and also at the upper inflection point where the hexa alcoholate is present. These samples were prepared by the addition of alcohol to the previously prepared salt. Since NiI_2 was so sensitive to air oxidation, the errors may be due to this, as the solid was exposed to air during the preparation, drying and weighing.

It was noted that the alcohol solution of nickel iodide changed from a red brown to a yellow green when the sample solution was cooled with a Dry Ice-acetone bath. This indicated a change in the solution composition and it was hoped that this presumably higher coordination numbered complex could be detected. It was thought that this complex might be the deca alcoholate because of the erratic results in this region. The solution was red brown at 0° . The vapor pressure of ethanol at 0° is small so measurements are more in error but there was no sign of the complex. For these results, see table 6 and figure 5.

TABLE 4

Vapor pressure-composition data for the nickel iodide-
ethanol system at 25°C

Determination #1

Mmole ethanol	Mmole ratio $\text{C}_2\text{H}_5\text{OH}/\text{NiI}_2$	Vapor pressure in mm. Hg
20.915	17.953	54.78
17.953	14.815b	52.40
14.860	12.716	49.40
13.518	11.603a	45.30
12.640	10.849	41.72
11.742	10.079	41.76
11.532	9.897	-----
8.793	7.548	35.78
6.725	5.773	22.88
4.852	4.643	22.72
3.461	2.969	22.80
2.804	2.400	22.50
2.213	1.896	21.86
1.174	1.007	21.80
0.690	0.597	20.46
0.400	0.343	17.50

Mmole NiI_2 1.165

a. solid separates (white)

b. solid appeared and redissolved

TABLE 5

Vapor pressure-composition data for the nickel iodide-
ethanol system at 25°C

Determination #2

Mmole ethanol	Mmole ratio $\text{C}_2\text{H}_5\text{OH}/\text{NiI}_2$	Vapor pressure in mm. Hg
24.450	23.737	55.48
14.608	14.183b	48.80
12.732	12.361	44.52
12.333	11.973a	44.86
11.311	10.971	42.20
10.095	9.795	39.26
9.087	8.822	37.18
8.252	8.011	35.98
7.493	7.274	32.12
6.650	6.456	27.06
5.991	5.816	23.06
4.704	4.567	22.56
3.795	3.684	22.36
2.465	2.393	22.86
1.917	1.861	21.76
1.232	1.196	19.80
0.813	0.789	19.00

Mmole NiI_2 1.167

a. Solid precipitates (white)

b. Solid appeared and redissolved

FIGURE 4
Vapor Pressure Composition
Curve
for the

C_2H_5OH/NiI_2 System at $0^\circ C$

Run 1 O

Run 2 X

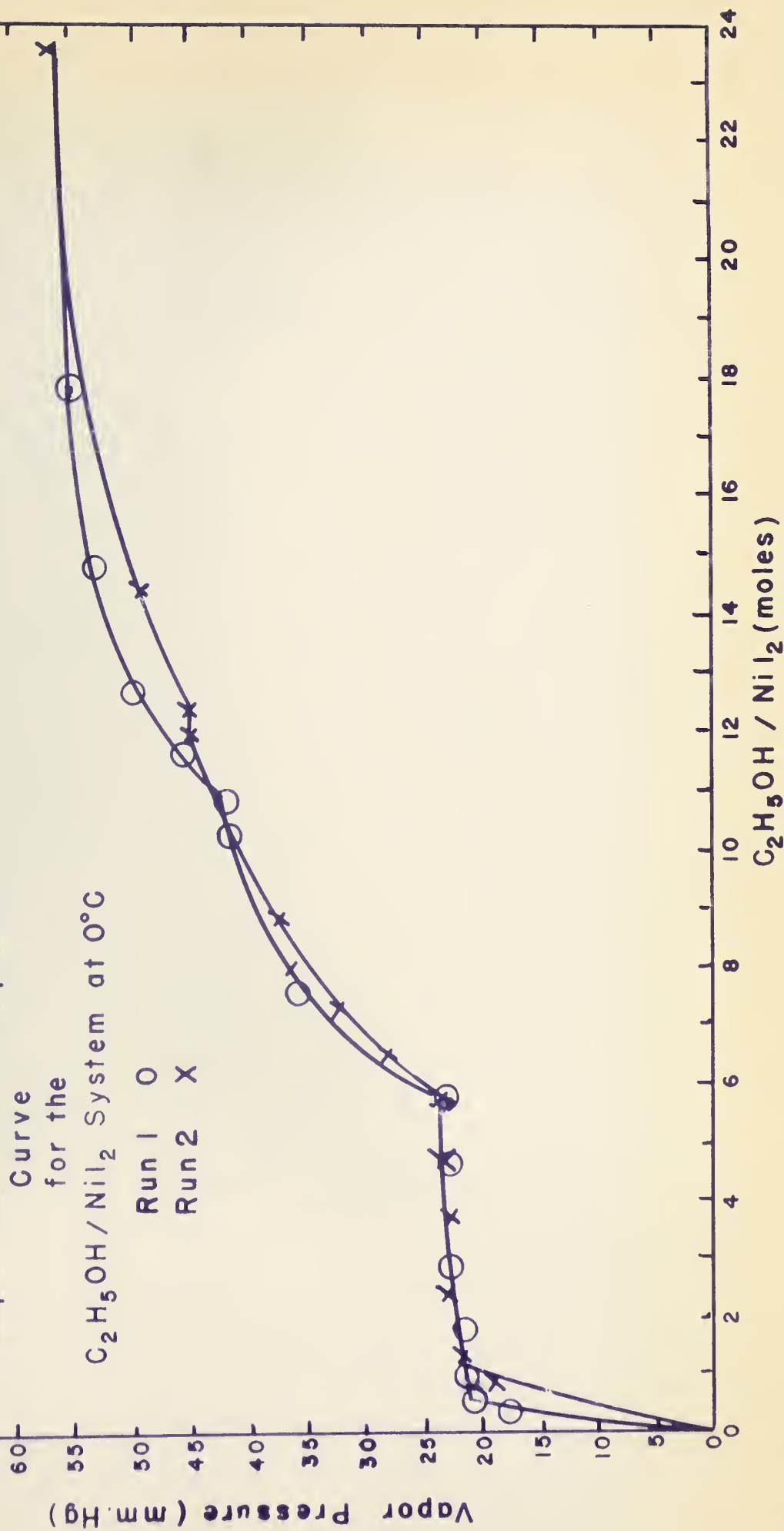


TABLE 6

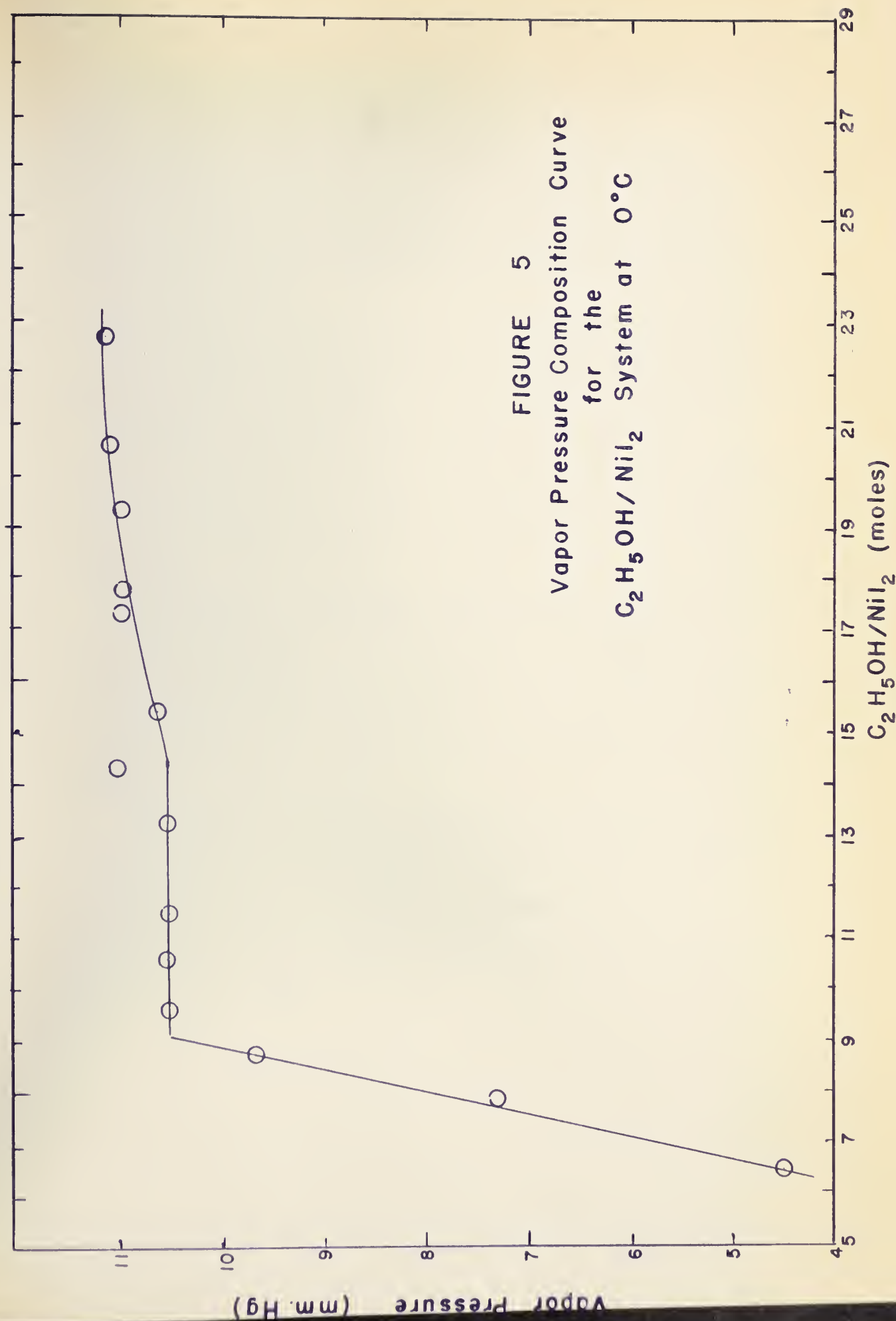
Vapor pressure-composition data for the system nickel
iodide-ethanol at 0° C

Mmole ethanol	Mmole ratio $\text{C}_2\text{H}_5\text{OH}/\text{NiI}_2$	Vapor pressure in mm. Hg
22.404	22.814	11.24
20.313	20.684	11.18
18.978	19.361	10.96
17.607	17.929	10.96
17.115	17.428	10.98
15.219	15.494a	10.62
14.000	14.256	11.00
13.050	13.289	10.50
11.400	11.608	10.50
10.519	10.712	10.50
9.469	9.643	10.50
8.687	8.846	9.68
7.739	7.880	7.34
6.139	6.252	4.46
5.639	5.742	5.12

Mmole NiI_2 0.982

a. Solid precipitates (white)

FIGURE 5
Vapor Pressure Composition Curve
for the
 C_2H_5OH/NiI_2 System at $0^\circ C$



During a typical run at 25° C, three differently colored solids were observed;

(1) White solid

(2) Deep red solid - Formed by decomposition of (1) and present exclusively at the point where all liquid disappeared.

(3) Black solid - Formed by decomposition of (2) and apparently represents the first stable alcoholate.

Samples prepared by the procedure where the salt was synthesized on the vacuum line gave consistent results. The data are shown in tables 7 and 8 and figure 6.

An arrest in the curve indicates the appearance of a new phase. In both runs, the appearance of the solid seemed to be transitory at a composition 15 mole ethanol per mole of NiI_2 and to be permanent only at a ratio of 12:1.

The other inflection points on the graph appear to be associated with ethanol NiI_2 complexes. These are shown to have the empirical compositions of 6 moles ethanol per 1 mole of NiI_2 and 2 moles ethanol per 1 mole of NiI_2 .

TABLE 7

Vapor pressure-composition data for the nickel iodide-
ethanol system at 25° C

Determination #3

Mmole ethanol	Mmole ratio $\text{C}_2\text{H}_5\text{OH}/\text{NiI}_2$	Vapor pressure in mm. Hg
18.428	18.746	55.12
16.944	17.684	53.12
15.395	16.019	52.78
15.454	15.721b	49.82
13.228	13.456	46.68
11.826	12.042a	46.58
10.448	10.629	46.16
9.509	9.673	45.12
8.496	8.642	43.54
7.787	7.922	41.92
6.540	6.653	34.36
6.201	6.308	29.38
5.884	5.986	22.86
5.474	5.569	21.50
3.929	3.997	21.50
2.647	2.693	19.00
2.297	2.337	16.60
1.888	1.921	16.10
1.140	1.160	15.32
0.228	0.232	9.32

Mmole NiI_2 0.961

a. Solid precipitates (white)

b. Solid appeared and redissolved

TABLE 8

Vapor pressure composition data for the nickel iodide-
ethanol system at 25° C

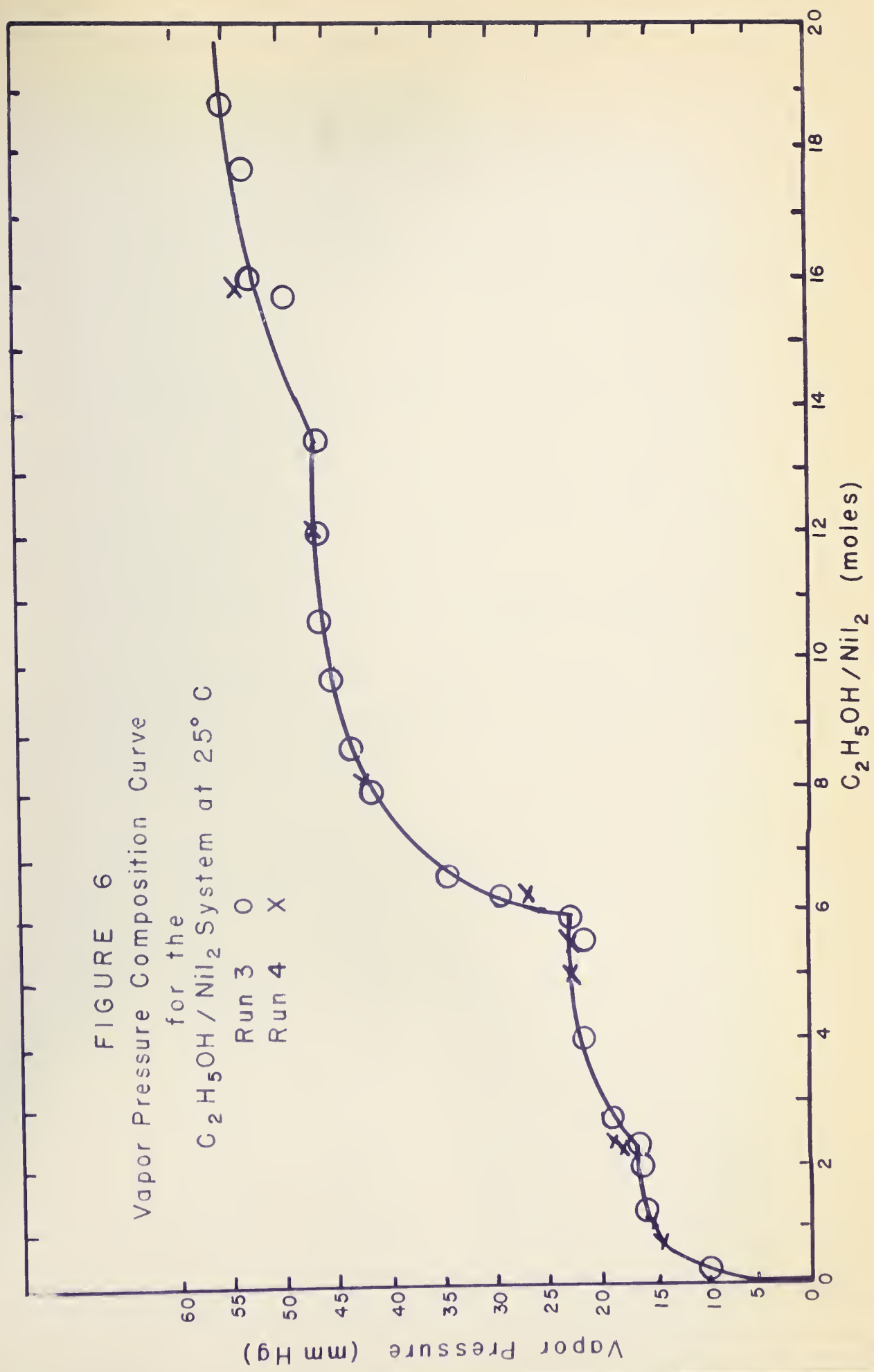
Determination # 4

mmole ethanol	mmole ratio $\text{C}_2\text{H}_5\text{OH}/\text{NiI}_2$	Vapor pressure in mm. Hg
15.446	16.070	53.60
11.570	12.039a	46.18
7.837	8.155	42.08
6.147	6.393	26.33
5.335	5.552	22.46
4.820	5.016	22.50
3.822	3.977	21.48
2.860	2.976	20.00
2.247	2.338	19.06
2.035	2.118	17.32
1.768	1.802	16.10
1.022	1.060	15.00
0.728	0.758	14.18

mmole NiI_2 0.983

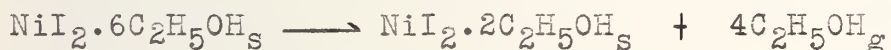
a. Solid precipitates (white)

FIGURE 6
Vapor Pressure Composition Curve
for the
 C_2H_5OH / NiI_2 System at $25^\circ C$
Run 3 O
Run 4 X



HEAT CALCULATION

The vapor pressure of the hexa alcoholate at different temperatures can be used with the Clausius-Clapeyron equation to determine the heat of vaporization of alcohol from the solid complex. The equilibrium in question was



The equilibrium constant for this reaction can be expressed as just the pressure over the solid. This is not exactly true but since the pressures are low, the errors will not be great.

$$\text{Therefore, } K_p = P^4 \text{ and then } \frac{d \log P}{dT} = \frac{\Delta H_v}{RT^2} \cdot$$

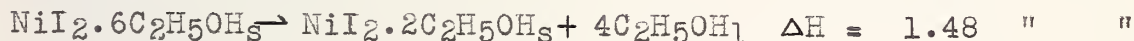
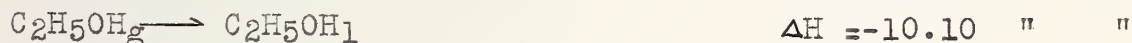
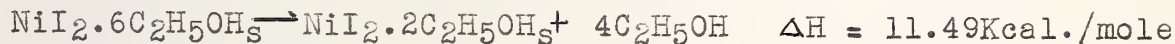
The variation of vapor pressure of $\text{NiI}_2 \cdot 6\text{C}_2\text{H}_5\text{OH}$ with temperature is shown graphically in figure 7 and the data are given in table 9.

TABLE 9

Heats of Vaporization of Ethanol

Pressure in mm. Hg	log P	$\frac{1}{T \times 10^3}$	Temperature in °K
14.06	1.1479	3.412	293.06
22.50	1.3522	3.354	298.16
23.34	1.3681	3.350	298.46
32.74	1.5150	3.298	303.16
35.70	1.5527	3.292	303.76
48.44	1.6852	3.246	308.07
53.00	1.7243	3.238	308.76

From the slope of the line in figure 7 it can be calculated for the equilibrium reaction (1) that $\Delta H_v = 11.49$ Kcal./mole.



The variation in vapor pressure of the dialcoholate with temperature was not determined.

Nickel iodide-diethyl ether system

Since the reaction of iodine and nickel went to partial completion in diethyl ether, and because the mechanism for the reaction is thought to involve some complex formation, a vapor pressure composition analysis was deemed necessary. The results of this analysis are shown in tables 10 and 11.

These results indicate that no stable $\text{NiI}_2 \cdot \text{C}_4\text{H}_{10}\text{O}$ is found.

FIGURE 7
Log P as a function of Temperature
for the
 $\text{NiI}_2 \cdot 6 \text{C}_2\text{H}_5\text{OH}$ System

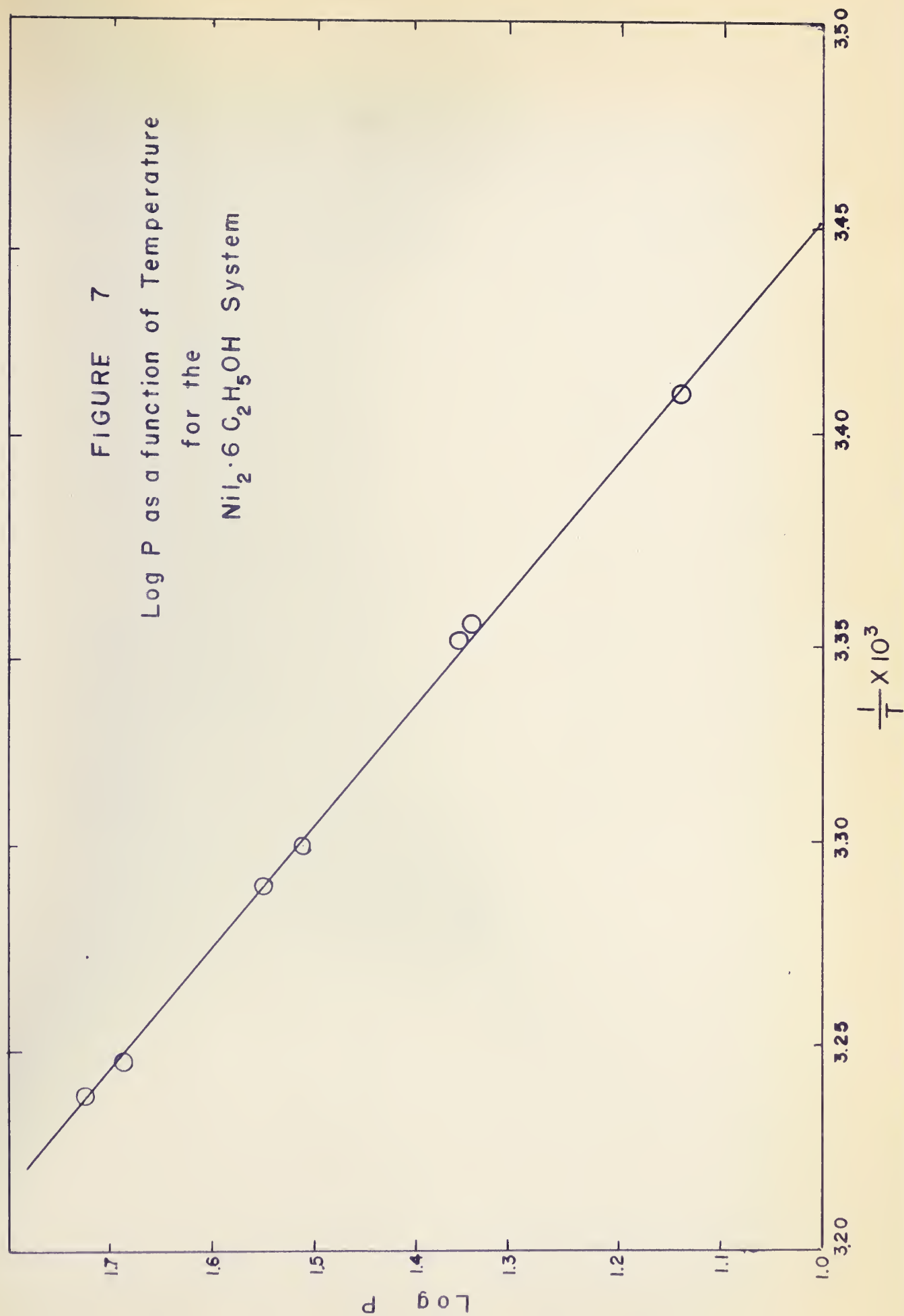


TABLE 10

Vapor pressure-composition data for the nickel iodide-diethyl ether system at 0° C.

Mmole ether	Mmole ratio $C_4H_{10}O/NiI_2$	Vapor pressure in mm. Hg
16.301	16.962	183.10
9.626	10.017	182.92
7.007	7.291	182.92
4.937	5.137	182.82
2.588	2.693	182.72
0.082	0.085	24.08

Mmole NiI_2 0.961

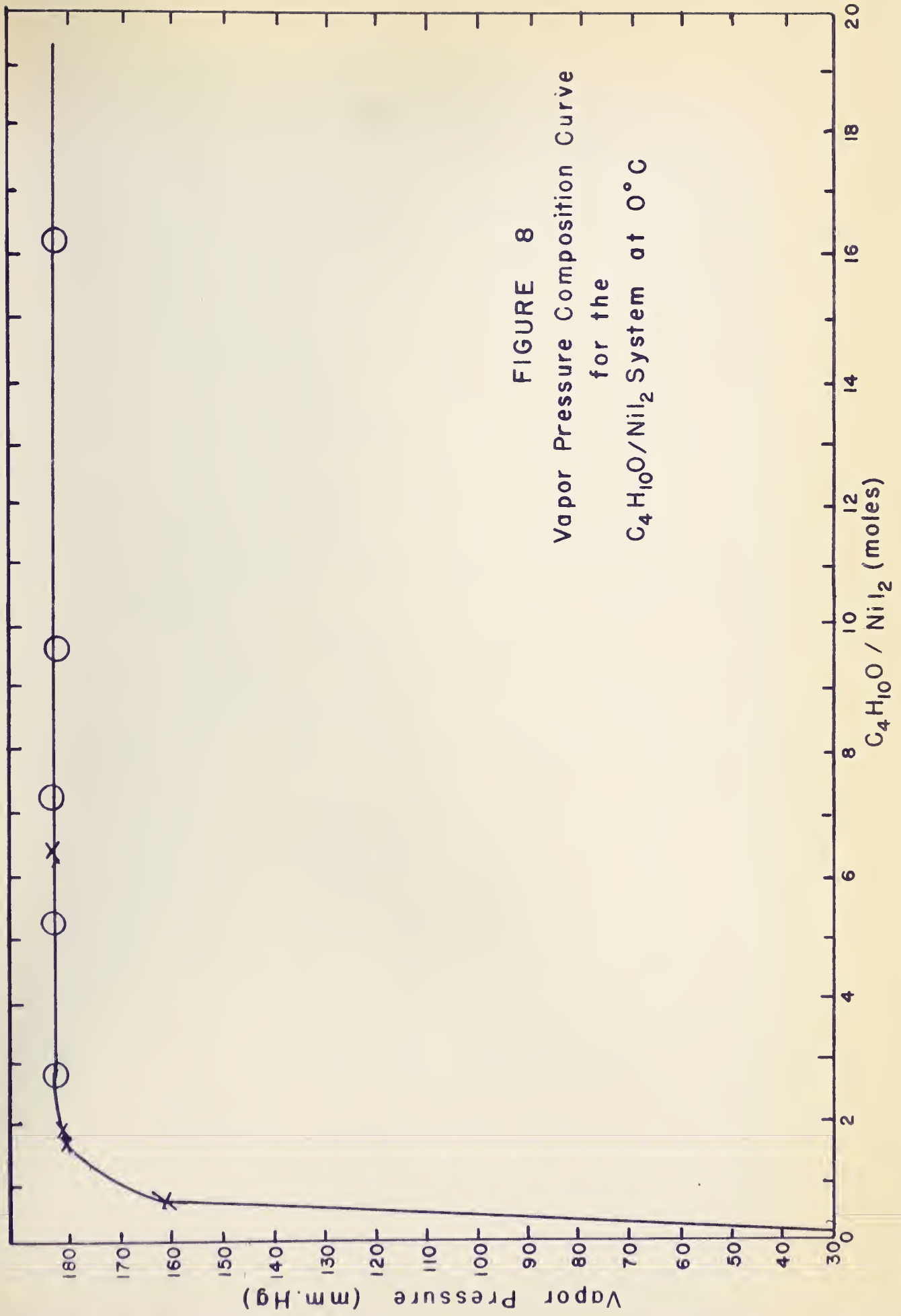
TABLE 11

6.194a	6.445	183.12
2.630a	2.737	181.64
2.153b	1.964	181.00
1.886b	1.721	181.00
0.754a	0.784	160.83

a. Mmole NiI_2 0.961

b. Mmole NiI_2 1.096

FIGURE 8
Vapor Pressure Composition Curve
for the
 $C_4H_{10}O/NiI_2$ System at $0^\circ C$



MOLECULAR WEIGHT CALCULATIONS

By use of Raoult's law it is possible to calculate the molecular weight of the salt in solution. Deviations from ideality are observed and an attempt has been made to compensate for these deviations by calculating the molecular weights on the basis of different assumed degrees of solvation.

- (1) No Complex
- (2) Di-alcoholate
- (3) Hexa-alcoholate
- (4) Deca-alcoholate.

The data obtained on each of these bases are shown in table 12.

TABLE 12

Molecular weights of NiI_2 in the system $\text{C}_2\text{H}_5\text{OH} - \text{NiI}_2$

Mmole ethanol	ΔP	$\frac{PW-W}{\Delta P}$	M_2^a 0-complex	M_2^a 2-complex	M_2^a 6-complex	M_2^a 10-c.
17.694	1.3	12.926	730.5	823	1105.0	1600
17.201	1.9	8.747	508	575	780	1214.6
16.711	2.4	6.860	410	466.3	640	1015
16.219	2.9	5.625	346.8	395.5	554	964
15.728	3.7	4.342	276.1	316.3	446	758
		NiI_2	.3072			
		Theoretical value		312.53		

CONDUCTIVITY MEASUREMENTS

Conductivity measurements were made on pure alcohol and on the same alcohol with 0.1 mmole of NiI_2 dissolved ^{Per} liter. These values are compared with those obtained in aqueous solution.

TABLE 13

Conductivity measurements and calculations on nickel iodide in ethanol

Sample	Cell constant	Specific conductivity	Equivalent conductivity
$\text{C}_2\text{H}_5\text{OH}$	2.54	2×10^{-6}	
$\text{C}_2\text{H}_5\text{OH NiI}_2$ (.1 mmole)	2.54	4.189×10^{-5}	20 Mho/equiv.
$\text{NiBr}_2 \cdot \text{H}_2\text{O}$ (.5 M)			73.4 " "

NICKEL BROMIDE ETHANOL SYSTEM

The difficulties encountered in the nickel bromide-ethanol system were essentially the same as those encountered in the nickel iodide-ethanol system. Data obtained from the early procedures are shown in tables 14 and 15 and figure 9. The procedure finally evolved was exactly that described earlier as giving the most satisfactory results for nickel iodide-ethanol system. The data obtained from this procedure in the NiBr_2 -ethanol system are shown in tables 16 and 17 and figure 10. Analysis of the salt obtained gave a molecular ratio of $\text{NiBr}_2 \cdot 0.020$

Nickel bromide-diethyl ether system

Similar results were obtained by the measurement of vapor pressure variation with composition for NiBr_2 in ether as were obtained for NiI_2 in ether. The results are in table 18 and figure 12.

TABLE 18

Vapor pressure-composition data for $\text{C}_4\text{H}_{10}\text{O}-\text{NiBr}_2$ at 0°C

Mmole ether	Mmole ratio $\text{C}_4\text{H}_{10}\text{O}/\text{NiBr}_2$	Vapor pressure mm. Hg
15.988	14.984	182.50
15.211	14.252	182.50
12.108	11.348	181.60
5.221	4.893	179.74
0.709	0.665	169.18

TABLE 14

Vapor pressure composition data^b for the nickel bromide-ethanol system at 25° C

Determination A

Mmole ethanol	Mmole ratio $\text{C}_2\text{H}_5\text{OH}/\text{NiBr}_2$	Vapor pressure in mm. Hg
65.240	18.326	50.22
58.290	16.373	42.60
50.091	14.072	46.06
42.993	12.081a	44.36
37.712	10.594	42.86
33.111	9.307	41.66
28.472	8.008	39.96
26.468	7.437	38.76
25.002	7.020	38.20
23.671	6.659	37.40
21.603	6.077	34.02
20.082	5.642	24.92
17.354	4.875	14.64
15.783	4.438	5.56
13.462	3.782	5.54
9.868	2.777	3.98
7.850	2.204	3.26
6.522	1.832	3.76
4.773	1.344	1.78
3.962	1.113	0.00

A. Solid separating

B. Data obtained by procedure #1

Mmole NiBr_2 3.560

TABLE 15

Vapor pressure-composition data ^b for the nickel bromide-ethanol system at 25° C

Determination B

Mmole ethanol	Mmole ratio $C_2H_5OH/NiBr_2$	vapor pressure in mm. Hg
18.791	15.550	49.44
15.683	12.982	43.56
13.843	11.464a	38.10
11.526	9.549	34.44
10.999	9.108	36.30
10.528	8.716	36.30
9.547	7.905	30.72
8.956	7.413	27.00
8.494	7.032	16.98
7.693	6.361	16.16
7.428	6.146	12.26
6.964	5.760	7.64
4.683	3.875	4.38
4.252	3.521	3.50

a. Solid separates

b. Data obtained by procedure #1

mmole $NiBr_2$ 1.208

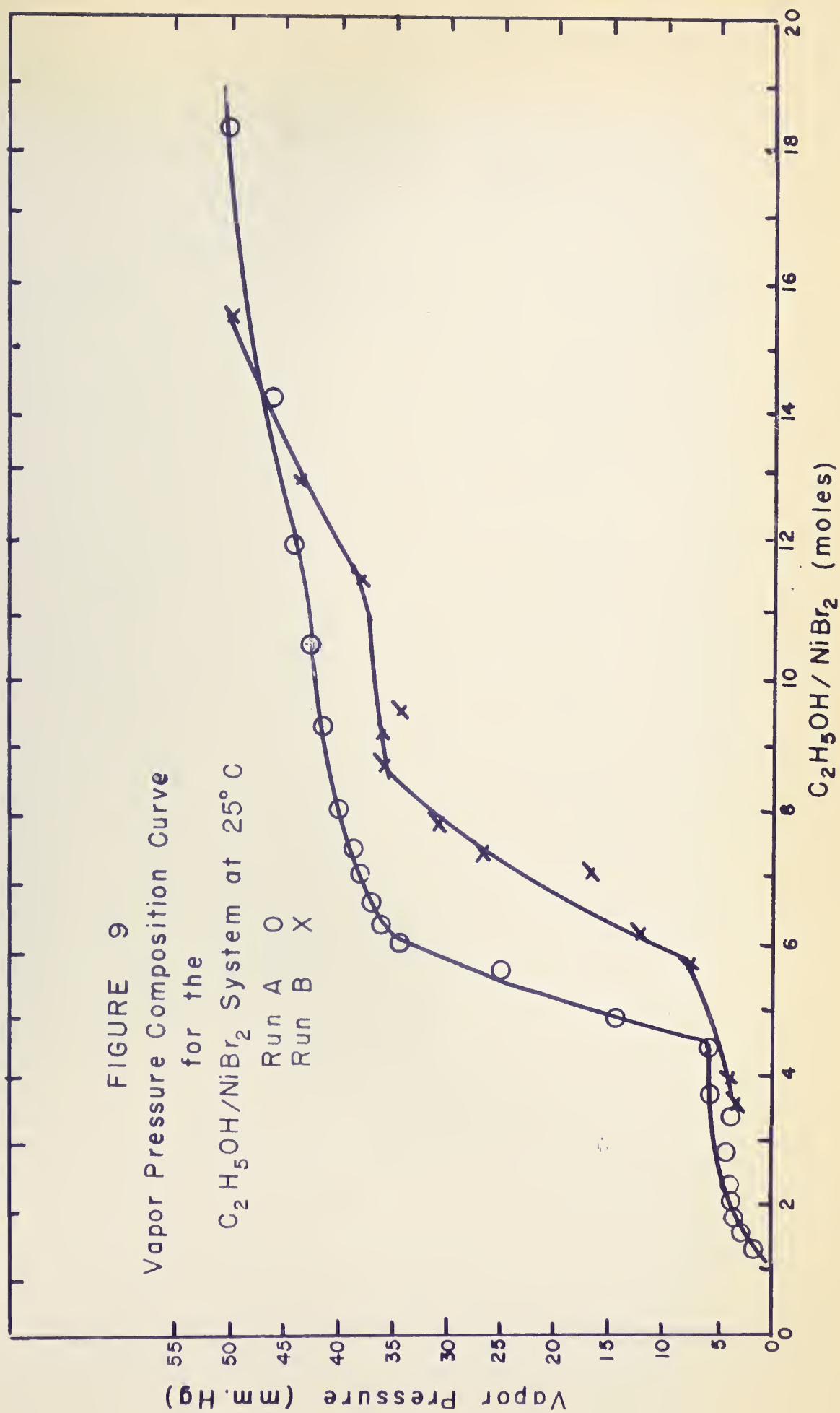


TABLE 16

b

Vapor pressure-composition data for the system

nickel bromide-ethanol at 25° C

Determination # 1

Mmole ethanol	Mmole ratio $\text{C}_2\text{H}_5\text{OH}/\text{NiBr}_2$	Vapor pressure in mm. Hg
22.370	20.965	53.66
17.400	16.307	51.20
15.198	14.244	51.36
14.004	13.125	48.98
13.007	12.190a	48.98
10.208	9.567	49.00
7.740	7.254	48.74
5.623	5.270	47.56
3.283	3.677	17.50
2.938	2.754	11.70
2.743	2.570	9.70
2.114	1.981	10.35
1.990	1.865	6.24
1.858	1.748	6.20

a. Solid separates

b. Data obtained by final procedure

mmole NiBr_2 1.067

TABLE 17

vapor pressure-composition data^b for the nickel bromide-ethanol system at 25° C.

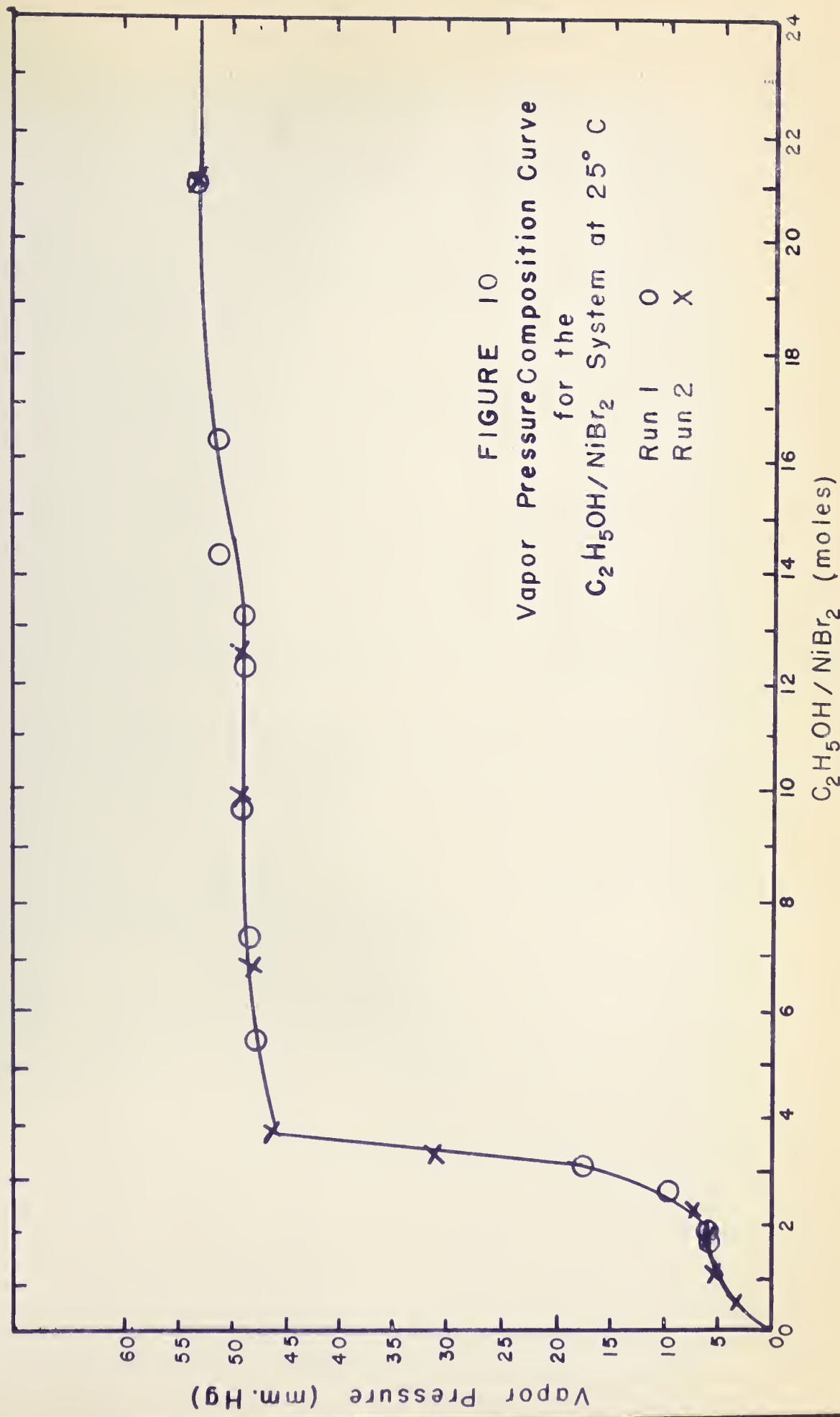
Determination # 1

MMoles	Mmole ratio C ₂ H ₅ OH/NiBr ₂	Vapor pressure in mm. Hg
21.537	20.186	55.32
16.207	15.189	51.78
13.326	12.489	49.40
10.476	9.818a	49.16
7.197	6.745	48.14
3.999	3.748	46.20
3.590	3.365	31.16
2.410	2.259	7.04
1.973	1.849	6.20
1.107	1.037	5.00
0.672	0.630	3.86

a. Solid separates

b. Data obtained by final procedure

Mmole NiBr₂ 1.067



Heat of Dissociation of Nickel Bromide Dialcoholate

For the reaction

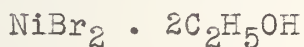


$$K_p = P^2$$

The variation of $\log K_p$ with temperature is shown in table 19 and figure 11.

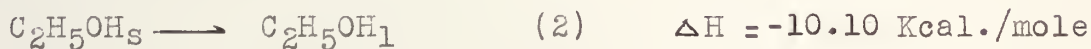
TABLE 19

Variation of $\log K_p$ with temperature for the compound



Pressure in mm. Hg	Log P	$\frac{1}{T \times 10^3}$	Temperature in °K
6.20	0.7924	3.354	298.2
12.02	1.0798	3.297	303.3
22.08	1.3439	3.245	308.2

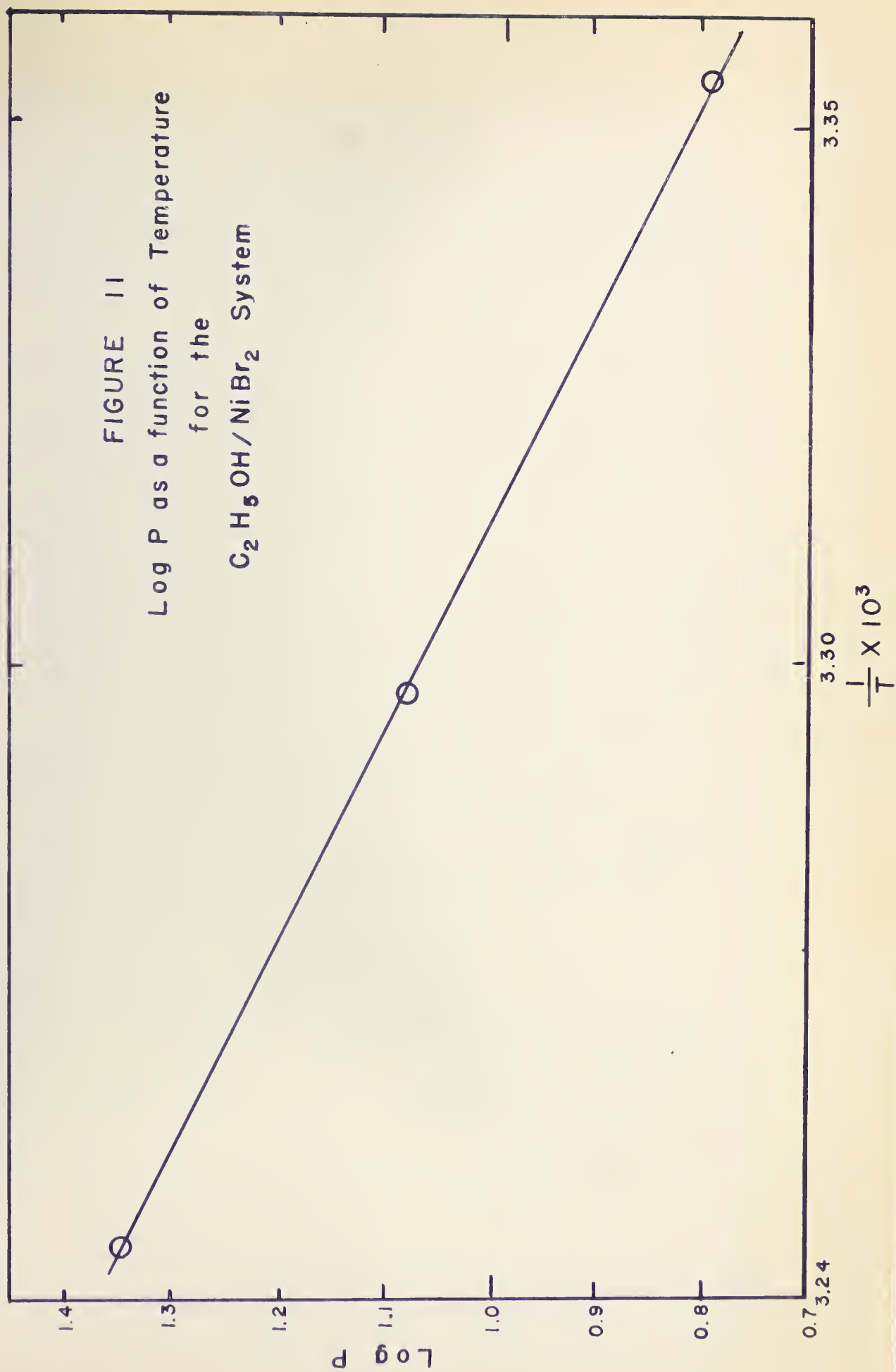
From the slope of the line in figure 11, ΔH_v for the equilibrium $\text{NiBr}_2 \cdot 2\text{C}_2\text{H}_5\text{OH}_s \longrightarrow \text{NiBr}_2_s + 2\text{C}_2\text{H}_5\text{OH}_g$ (1) is 27.35 Kcal./mole.



$$\Delta H = 17.25 \text{ Kcal./mole}$$

This value is of the same order as the heat of hydration for the same salt in water. It is 19.1 Kcal./mole. (17)

FIGURE II
Log P as a function of Temperature
for the
 $C_2H_5OH/NiBr_2$ System



MOLECULAR WEIGHT CALCULATIONS FOR NICKEL BROMIDE
IN ETHANOL

Molecular weight of NiBr_2 in ethanol calculated from Raoult's on the basis of vapor pressure lowering are shown in table 20.

TABLE 20

Molecular weight calculation for NiBr_2 in ethanol

Mole ethanol	ΔP	$\frac{PW-W}{\Delta P}$	M_2 O-complex	M_2 2-complex	M_2 6-complex
18.139	3.5	3.490	192.8	216.7	288.2
17.605	4.5	2.669	151.6	171	229.9
17.072	5.3	2.231	130.7	148	201.5
16.538	5.7	2.058	124.4	141.5	195.3
16.005	6.5	1.7758	110.9	126.7	177.6

Molecular weight NiBr_2 218.53

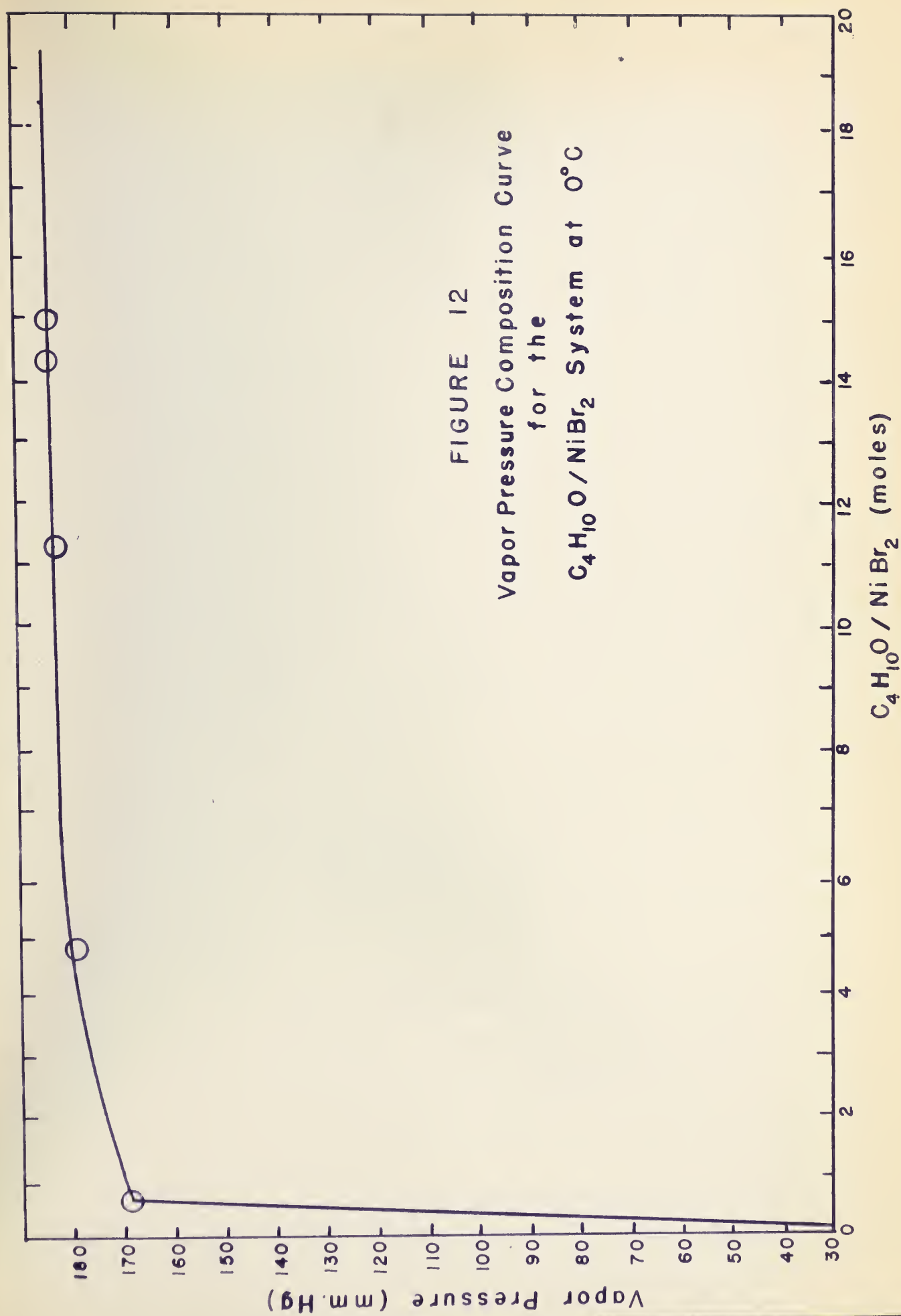
CONDUCTIVITY MEASUREMENTS FOR NiBr_2 IN ETHANOL

Similar values were obtained for NiBr_2 in ethanol as were obtained for NiI_2 in ethanol. The data are shown in table 21.

TABLE 21

Sample	Cell constant	Specific conductivity 2×10^{-6}	Equivalent conductivity -----Mho/equiv.
$\text{C}_2\text{H}_5\text{OH}$	2.54		
$\text{C}_2\text{H}_5\text{OH NiBr}_2$	2.54	5.08×10^{-5}	18.5 Mho/equiv.
$\text{H}_2\text{O NiBr}_2$ (.5M)			73.4 Mho/equiv. (18)

FIGURE 12
Vapor Pressure Composition Curve
for the
 $C_4H_{10}O / NiBr_2$ System at $0^\circ C$



DISCUSSION

PART 1

The procedure developed for the preparation of the anhydrous nickel halides by the reaction of the metal with the corresponding halogen seems to hold great promise as a general synthetic method. The single disadvantage of the procedure would seem to be the side reactions with the solvent.

Unfortunately, the side reactions in the preparation of nickel bromide were many. The formation of acet-aldehyde and the possible oxidation of this to the acid are but two of the possible reactions. However, the concentration of these side reaction products can be reduced. The addition of toluene and the subsequent distillation of the azeotrope effectively removes.

The analysis of samples of nickel bromide and iodide prepared in contact with the air were all low, whereas those samples prepared out of contact with air on the vacuum line gave analysis of 99 % purity. It was concluded then that the discrepancies were due to air oxidation.

Then, for most purposes samples prepared in air or nitrogen will suffice. However, for precise work samples should be prepared out of contact with air.

PART 2

The stable alcoholates formed by NiI_2 are of the same coordination number as the coordination number of the amines formed by the salt, namely the six and two. Biltz (19) observed the dissociation of the hexaamine to the diamine to the anhydrous salt which are the identical steps observed in the $\text{NiI}_2 \cdot 6\text{C}_2\text{H}_5\text{OH}$ dissociation. It was interesting to note that no stable complexes were formed by NiI_2 in ether.

Nickel bromide only formed a stable dialcoholate, in contrast to the 9, 6, 4 and 2 hydrates reported in the literature. The possibility of an unstable hexa-alcoholate is indicated by the molecular weight calculations. NiBr_2 also showed no tendency to form stable complexes, with ether.

The alcohol complexes formed by these two salts can be partially explained if the anion sizes are considered. If the salts are ions in solution, there would be solvation of the ions. The iodide ion, being larger than the bromide ion, would have more space around it for solvate molecules. Very weak bonds are formed in these solvate spheres. As the concentration of the solution increases the ions recombine to form molecules and some of the solvated molecules are lost. The iodide would be able to hang on to more of these solvated molecules than the bromide, because of its larger size.

The heat of dissociation of a complex involving iodide solvent bonds would be small. The $\text{NiI}_2 \cdot 6\text{C}_2\text{H}_5\text{OH}$ dissociated to the dialcoholate which is probably more stable, because it forms the normal coordination number of nickel, four.

NiBr_2 as a dialcoholate is a stable complex of nickel. The heat of dissociation is comparable to the heat of dissociation of the dihydrate which is 19.0 Kcal./mole. (20) The steric requirements for a hexa-alcoholate probably such that it is only stable in solution.

The molecular weight calculations all seem to trend in the wrong direction. If the compounds, NiI_2 and NiBr_2 are dissociated to any extent in solution, an upward trend in the calculated molecular weights would be expected as the solution became more concentrated, because association would be increasing. As ions the ions are acting as individual molecules and the effective lowering of the vapor pressure is greater than normal.

A decreasing in molecular weight values is noted in this work. Though speculation, there could possibly be a couple of reasons for this;

(1) A coordination number change of the nickel as the solution becomes more concentrated. The appear-

ance and redissolving of the solid in the range of 15 mole ethanol to 1 mole of the salt might indicate this. Obviously a transition of some sort is occurring here, but just what it is, is not easy to say.

(2) The conductance measurements indicate that the salts are not completely ionized. The ionization constant would be small but it is feasible that the type of solvation changes from an ion solvation in dilute solution to molecular solvation in more concentrated solution.

The conductance measurements themselves were disappointingly low. Because of the variation in molecular weights, it was expected that the two salts would be highly ionized and that a substantial argument could be built up. Such is not the case.

It is hoped that future work will be able to explain these seemingly abnormal results. Conductivity measurements are planned on these solutions, as they become more concentrated. This, it is hoped, would show any change in the solution which would influence the solvation.

Another piece of work which would give valuable information would be x-ray measurements on the solid transitions observed. This would tell us what solvate the white solid is.

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